

Adsorption of Basic Dyes Crystal Violet on Agricultural Biomass: Characterization, Isotherm and Kinetic Studies

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DOI: <https://doi.org/10.30880/ijie.2022.14.01.025>

Received 25 April 2021; Accepted 28 September 2021; Available online 07 March 2022

Abstract: The removal of crystal violet (CV) dye from aqueous solution using agricultural waste-based adsorbent was investigated. Two adsorbents, lime peels (*Citrus aurantifolia*) and pineapple leaves (*Ananas comosus*) at different quantities (1, 3, 5, 7 and 10 g) were tested to 50 mL of CV solution (1,000 mg/L) at 3-hours interval incubation. The characterization of adsorbents was performed by FESEM and FTIR to explain adsorbent's properties and structure. The results showed that lime peels and pineapple leaves removed 98% and 97% of CV dye, respectively. Under FESEM analysis, the surface structure of adsorbent that perforated and the presence of polymer were attributable to the adsorption ability. Indeed, FTIR analysis confirmed the attendance of carboxyl and carbonyl group that caused the enhancement of adsorption process.

Keywords: Crystal violet, basic dye removal, agricultural based-adsorbent

1. Introduction

Water contamination is one of the significant issues faced by many countries in the world. Many organic and inorganic pollutant had been found in aquatic ecosystem due to waste disposal of various elements from agriculture, industry and mining [1], [2]. Synthetic dye is one of most concern pollutants since its increasing in usage for industrial purposes lead to its high abundance in the water environment. These included due to the rapid development of rubber, textile, paper, plastic, leather and food technology. The high amount of water usage for dyeing process have resulted in expendables mixture of natural and synthetic dyes, e.g., nitro, azo, methane and carbonyl that resistant to the biodegradation. In addition, the adverse health effect resulted by the utilization of dyes might be arise due to its carcinogenic properties [2]. Moreover, the aquatic organisms that require oxygen and sunlight for living will be suffocated because high color and COD content in the water.

The water contaminated with dye requires an effective and an efficient treatment to dismiss the environmental threat. Up to now, various methods and approaches successfully eliminated the dye molecules, including ion-exchange, coagulation-flocculation, electrochemical, ozonation and adsorption. Amongst, adsorption was mostly chosen since it displayed high removal capability [3]. Adsorption uses adsorbent materials, composed of activated carbon which is expensive and limit to certain dye. Therefore, the need of novel adsorbent as alternative is highly demanded. Many researches on adsorption have demonstrated the removing process of dye [4]-[6] generate three by product such as activated carbon, carbonaceous adsorbents and polymeric adsorbents. Overall, activated carbon was widely used [7],

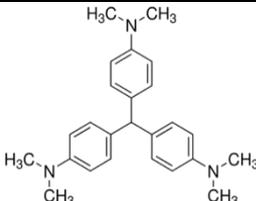
cause their multi functions, as wide variety of dyes removal and various kinds of pollutants (phenols, pesticides, PCBs, chlorinated hydrocarbon, detergents, metal ions, and other taste- and odor- producing compounds) removal [8]. The use of activated carbon from carbonaceous raw materials such as agricultural waste for treating a wastewater containing dye has long been pointed out as very promising material source. These include bagasse, pith of coir, banana and date, sago, silk cotton hull, cob of corn and maize, rice husk, sawdust, bamboo, peel of cassava, orange, jackfruit, rambutan, durian, and mangosteen, empty fruit bunch and spent tea leaves [3], [9], [10]. However, lack information for reactive dye particle, CV. In this study, the removal rate and adsorption capacity of CV was investigated using two agricultural waste, lime peels (*Citrus aurantifolia*) and pineapple leaves (*Ananas comosus*). The variables on adsorption process performance e.g., adsorbent dosage and adsorption period, were also examined. In addition, Field Emission Scanning Electron Microscopy (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR) were performed for characterizing the chemical and texture of adsorbents.

2. Materials and Methods

2.1 Adsorbent and Dye Preparation

The seed of pineapple peel and lime peel were cleaned and form a small shape, oven at 105°C for up to 2 days and formed a powder and adsorbent was ready to use for experiment. Crystal Violet (CV) was obtained from Sigma Aldrich, Malaysia then dissolved 1 gram of CV in 1,000 ml distilled water to obtain a 1,000 mg/L CV stock solution. The solution was then store at room temperature until ready to use for adsorption experiment. Table 1 shows the chemical structure of CV.

Table 1 - Physical and chemical characteristics of CV

| Dye | CV |
|--------------------|---|
| Chemical Structure |  |
| Synonym | Basic violet 3 |
| Appearance | Crystalline powder |
| Physical State | Solid |
| Solubility | Soluble in water |
| Melting point | 205 °C (401 °F; 478 K) |
| Molecular Weight | 407.979 g mol ⁻¹ |
| Molecular Formula | C ₂₅ N ₃ H ₃₀ Cl |
| Max. Wavelength | 590 nm |

In order to obtain the working solution, specific amount of deionized water was added to 1,000 mg/L CV stock solution. Using 100 mL-Erlenmeyer flasks, 50 mL CV dye solution supplemented with a variety of adsorbent dosage (1, 3, 5, 7 and 10 g) were agitated at 120 rpm in 25°C. Then filter it by using the cellulose membrane size of 0.45 µm (Agilent Technologies, Germany). The CV dye removal ability of PL and LM were measured every 3 h until 24 h. The detailed of experimental conditions are summarized in Table 2.

Table 2 - Various experimental conditions on the adsorption of CV

| | Parameters | | | |
|-----------------------------|------------|--------------------------|----------------------|------------------|
| | pH | Dye concentration (mg/L) | Adsorbent dosage (g) | Temperature (°C) |
| Effect of pH | 3-8 | 50 | 5 | 28 |
| Effect of dye concentration | 6 | 25-125 | 5 | 28 |
| Effect of adsorbent dosage | 6 | 50 | 1-9 | 28 |
| Effect of temperature | 6 | 50 | 5 | 4-40 |

2.2 Adsorption Experiment

The batch experiment of CV adsorption ability by using pineapple peel and lime peel were performed in 100-mL conical flask which consist of 5 grams adsorbent and 50 mL of CV dye solutions (1,000 mg/L). All flasks were agitated at 120 rpm in 25°C for 12 h until a normal balanced state was reached. Suspensions were removed by 0.45 µm cellulose membrane filter and supernatant was put through to Uv-Vis Spectroscopy (MACHEREY-NAGEL Spectrophotometers NANOCOLOR® VI) in order to measure the remaining of the CV dye concentration. The following equations (1 and 2) were used to measure percentage of CV dye removal and capacity of adsorption (mg/g):

$$\text{Color Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

$$\text{Adsorption capacity} = \frac{C_o - C_e}{X} \times V \quad (2)$$

where C_o and C_e are the CV concentration at early and normal balance state (mg/L), V represents liters of dye solution (L), and X is the grams of adsorbent (g) used in the experiment.

2.3 Adsorption Characterization

The adsorption characterizations were determined by two approach, Field Emission Scanning Electron Microscopy (FESEM, JEOL 6335f-SEM, Japan) and Fourier Transform Infrared Spectroscopy (FTIR). FESEM specifically to elucidate the role of surface texture and morphology during adsorption process. While FTIR exhibited the properties of functional groups at spectra range of 400 – 4000 cm^{-1} (Perkin Elmer, USA) that existed in the surface of adsorbent early and end of decolorization process.

3. Results and Discussion

3.1 Batch Studies

Fig.1(a) shows the CV adsorption of pineapple leave (PL) and lime pineapple (LP) at the initial concentration of 25 – 125 mg/L. The CV removal were decreased from 98% to 34% and 97% to 23% for PL and LP, respectively, as the increased initial CV concentration. Meanwhile, the capacity of adsorption rose from 8.3 to 13.2 mg/g (PL) and 7.9 to 12.8 (LP). When the outer surface of adsorbents had reached saturation stage, the vacant sites trapped the CV dye ion on their surface, resulted in the varied of obtained results. However, the ratio of adsorbent to adsorbent is low at 125 mg/L concentration, led to decreasing removal percentage. Mostly, adsorption that comprised the surface reaction in the early adsorption process were fast [11]-[13].

Fig. 1(b) display the adsorption capacity under different PL and LM dosage of 1, 3, 5, 7 and 9 g. It showed that the removal rate of PL and LP were slightly rose concomitant with the increased of adsorbent to 5 g. The obtained removal percentage of CV increased from 54 to 95% and from 33 to 94 % for PL and LP, while the adsorption capacity decreased from 12.3 to 9.7 mg/g (PL) and 10.5 to 9.3 (LP) with an increase in the adsorbent dosage from 1 to 5 g. Above 5 g of adsorbent dose the sorption equilibriums of dyes were reached. To this point, the usage of 5 g adsorbent exhibited the highest capacity and suitable to treat CV. It was found that the efficiency of removal was not obtained at 7 and 10 g of adsorbents dosage. These corresponded to the increased surface area was followed by the increased adsorbent dosage led to rise active area of adsorbent [6], [14]-[16].

As it might disturb the adsorbent surface loading and the level of dye ionization, pH is a critical factor for optimal adsorption process as shown in this study (Fig. 1(c)). The increased of pH have resulted in increased CV dye adsorption. Adsorption of PL were 45 to 95% at pH of 3 to 6. Above pH of 6, the adsorption process was remained constant. In the case of LP, pH did not affect to the CV dye adsorption. At pH below 5, increasing the ionic strength in the system, would decrease the adsorption capacity. About 77 to 94 % were absorbed during the experiment. The results are similar with previous studies [6], [15], [16].

The effect of temperature on PL and LP sorption onto CV was conducted at concentration of 50 mg/L, 5 g of adsorbent and pH 6 (Fig. 1(d)). The removal of CV decreases rapidly from 34 to 95% and 23 to 94% for PL and LP when the temperatures escalated from 4 to 28°C. The removal was suddenly decreased when temperature increases to 40°C (65 and 59% for PL and LP). These suggested that at the room temperature, the optimal CV adsorption by PL and LP were obtained. Our result is similar with previous studies reported [17]-[18]

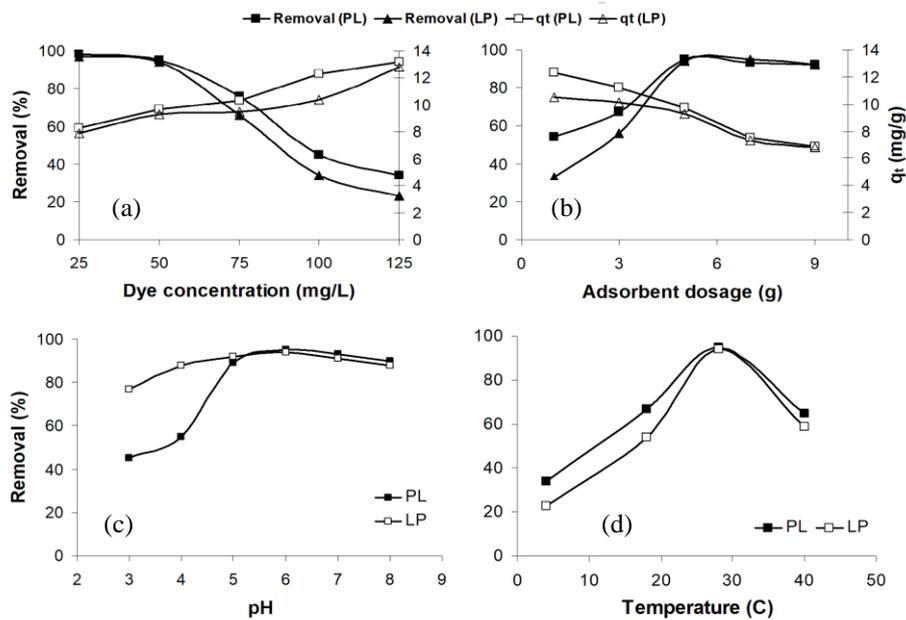


Fig. 1 - Effect of some parameter on adsorption of CV dye: (a) dye concentration; (b) adsorbent dosage; (c) Ph; (d) temperature

3.2 Characterization of The Adsorbents

Fig. 2 illustrates the study of the PL and LM's surface texture and morphology, prior to and during the adsorption process. The figure showed that PL has a perforated surface structure. It is clearly shown that the surface structures of PL are cellulose-based material tannin and lignin based organic compounds. LP has visible pores with the absence of polymer compounds, deep pores than bark. However, the pores did not have ability to trap CV dye particle. Similar findings from prior research indicate that polymeric adsorbents can enhance the adsorbent's ability to capture dye particles resulting in the removal of CV dye particles from the aqueous solution [3]. After the adsorption process, CV dye particle was found inside pores and in the midst of cellulose and hemicellulose. Other polymer component in the biomass such as lignin played a key role as the dye particles's glue. Hence, the pores and polymer component has been proven to play important role in locating the dye particles while clean up the contaminated water. Under FTIR studies, characterizations of PL and LP were measured at the range of 4000–400 nm functional groups (Fig. 3). The obtained peak represents the wide variety of functional group of chemicals inside both adsorbents, PL and LM. At the peak 3394.26 cm^{-1} and 2925.74 cm^{-1} , chemicals represented as group of O–H stretch, H–Bounded and C–H e.g., phenols and alcohols. Functional group from carbonyl, ester with N–H bend and amides with C–H rock were amounted at 1623.36 cm^{-1} and at 1390.18 cm^{-1} , respectively.

Table 3 - FTIR spectral characteristics of adsorbents

| PL frequency (cm^{-1}) | | Assignment | LP frequency (cm^{-1}) | | Assignment |
|-----------------------------------|---------------------|------------------------|-----------------------------------|---------------------|------------------------|
| Before adsorption | After adsorption CV | | Before adsorption | After adsorption CV | |
| 3393.26 | 3407.59 | O–H stretch, H bounded | 3393.09 | 3410.16 | O–H stretch, H bounded |
| 2925.74 | 2922.52 | C–H | 2929.01 | 2926.77 | C–H stretch |
| 1623.36 | 1630.43 | N–H bend | 1627.48 | 1628.03 | N–H bends |
| 1390.18 | 1374.84 | C–H rock | 1402.83 | 1436.87 | C–C stretch |
| 1058.14 | 1052.89 | C–N stretch | 1062.21 | 1064.10 | C–N stretch |
| 612.62 | 608.79 | C–Br stretch | 615.24 | 623.28 | –C≡C–H:C–H bends |

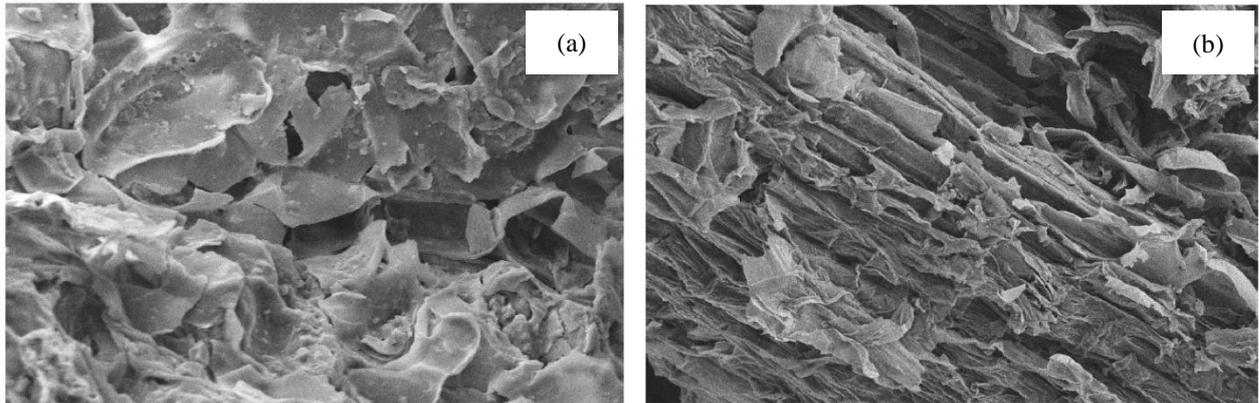


Fig. 2 - FESEM images of lime peel powder (a) and pineapple leaves powder; (b) after adsorption

In Fig. 3, from FTIR analysis of LP, the strong peak at 3393.09 cm^{-1} and 2929.01 cm^{-1} were identified as O–H stretch and H–bonded e.g., alcohols and phenols, respectively. The presence of N–H bend was obtained at peak of 1627.48 cm^{-1} . Functional group of amides with C–N stretch was at peak of 1062.21 cm^{-1} and amides with $\text{–C}\equiv\text{C–H:C–H}$ bends at peak of 615.24 cm^{-1} . The complexities of PL and LP were shown with the spectra number of their peaks (Table 3). By knowing the functional group, the binding mechanism of PL and LP were able to be explained. In this study, functional group existed in PL and LP were alcohols, phenol, carboxylic acid, carbonyl group and ether, which played significant role in binding or trapping of CV. The alteration of functional group before and after adsorption process explained how the functional group played important role during the adsorption of CV dye particles.

3.3 Adsorption Isotherm

Strong adsorption interaction between adsorbents and the CV dye particle were shown by the decreasing CV residual with a time. Table 4 displays prediction of the sorption potential of adsorbents, q_m value through plotting $1/q_e$ versus $1/C_e$ to the Langmuir isotherm. $\text{Log } q_e$ against $\text{Log } C_e$ define the values of K_F and n in the Freundlich isotherm and Temkin graphs, yielding a linear curve with a correlation factor (R^2). The Langmuir isotherm with R^2 values of 0.9945 and 0.9792, provided a more fitting result than Freundlich isotherm. It presumes that the adsorbent’s surface was homogenous that the data fit with Langmuir model. Additionally, it can be used to determine the monomolecular adsorption capacity, q_m or extended to which a monolayer covers the adsorbent’s surface and there is no lateral interaction between organic molecules or adsorbate when a single molecule occupied a single surface site [19].

Table 4 - Isotherm parameters for adsorption of CV onto PL and LP

| Adsorption isotherm | Adsorption constant | PL | LP |
|---------------------|---------------------|---------|---------|
| Langmuir | q_m (mg/g) | 9.7752 | 9.5057 |
| | K_L (mg/L) | 0.0078 | 1.6260 |
| | R^2 | 0.9945 | 0.9792 |
| Freundlich | n | 89.2857 | 40.3226 |
| | K_L (mg/g) | 10.1555 | 10.5609 |
| | R^2 | 0.9928 | 0.9820 |

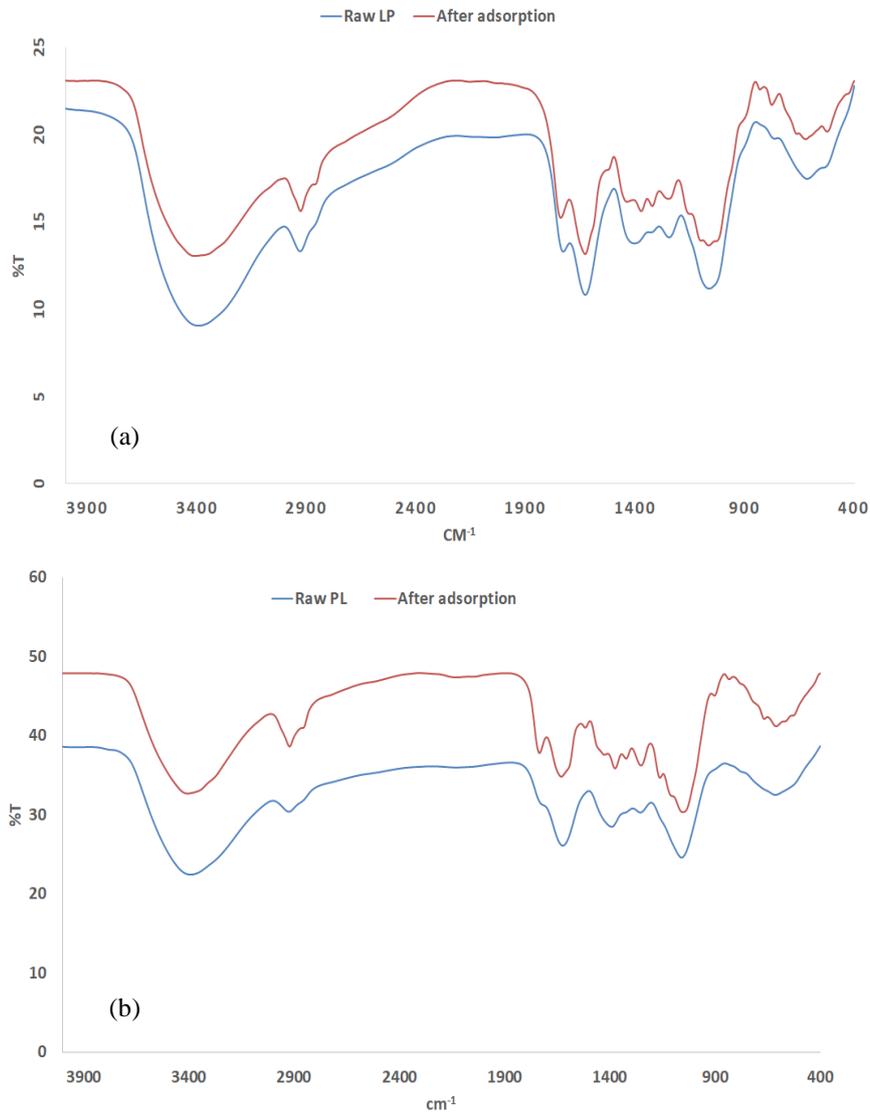


Fig. 3 - (a) FTIR adsorption peaks for lime peel powder and (b) pineapple leaves powder.

3.4 Adsorption Kinetics

By plotting graph $\ln(q_e - q_t)$ versus t for pseudo-first-order, t/q_t versus t for pseudo-second-order models and q_t versus $t^{1/2}$ for intraparticle diffusion models, kinetics rate constant, k and q_e can be calculated as shown in Table 5. The amount of dyes sorbed (q_e) in each experiment was found to be nearly identical to the amount calculated using pseudo second order models. The R^2 value obtained from pseudo second order models for each experiment were 1.000, indicating a better fit than that produced from pseudo-first-order and intraparticle diffusion models. This implies that the adsorption of CV pseudo second order.

Table 5 - Kinetic parameter of CV adsorption

| Adsorption Kinetics | PL | | | | LP | | | |
|-------------------------|---------------------|---------------------|--------|--------|---------------------|---------------------|--------|--------|
| | $q_{e, \text{exp}}$ | $q_{e, \text{cal}}$ | k_2 | R^2 | $q_{e, \text{exp}}$ | $q_{e, \text{cal}}$ | k_2 | R^2 |
| Pseudo-first-order | 9.9211 | 9.9322 | 0.0974 | 0.6254 | 9.7669 | 9.7925 | 0.0337 | 0.9983 |
| Pseudo-second-order | 9.9211 | 9.8619 | 2.7058 | 1.000 | 9.7669 | 9.7752 | 1.9380 | 1.000 |
| Interparticle diffusion | 9.9211 | 9.8981 | 0.019 | 0.3854 | 9.7669 | 9.7575 | 0.0175 | 0.8105 |

4. Conclusions

Attempts on the treatability of CV dye solution was demonstrated using low cost adsorbent from agricultural waste. Two adsorbent agents exhibited close to 100% of CV dye removal. With 5 g adsorbent, the accelerated adsorption capacity was obtained but impractically for 7 and 10 g adsorbent dosages. The highest result was found to be 13.2 and 12.8 mg/g for PL and LP, respectively. The increased of pH have resulted in increased CV dye adsorption. Adsorption of PL were 45 to 95% at pH of 3 to 6. The removal of CV decreases rapidly from 34 to 95% and 23 to 94% for PL and LP when the temperatures escalated from 4 to 28°C. It is shown that the surface structures of PL are cellulose-based material tannin and lignin based organic compounds. LP has visible pores with the absence of polymer compounds, deep pores than bark. However, the pores did not have ability to trap CV dye particle. The functional group presented in PL and LP were alcohols, phenol, carboxylic acid, carbonyl group and ether, which played significant role in binding or trapping of CV. Under these circumstances, the PL and LP might be good alternative for treating water contaminated with dye particles, especially CV.

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